

PATENT SPECIFICATION

937,750

NO DRAWINGS.

937,750



*Date of Application and filing Complete Specification :
Sept. 23, 1959. No. 32331/59.*

*Application made in United States of America (No. 762,951) on
Sept. 24, 1958.*

Complete Specification Published : Sept. 25, 1963.

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Index at Acceptance :—Classes 1(2), AD41, AG12D41 ; and 1(1), A3B1.

International Classification :—C01g (B01j).

COMPLETE SPECIFICATION.

Metal Loading of Molecular Sieves.

We, UNION CARBIDE CORPORATION, of 270 Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America (assignee of Donald Wesley Breck and Robert Mitchell Milton), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing metal-loaded zeolitic molecular sieves which are suitable for use as catalysts, scavengers and getters.

The use of metals, as catalysts, scavengers, and getters in a number of chemical reactions and chemical systems is well known to the art. The effectiveness of the metal in such cases has been found to depend, to a considerable degree, on the form in which the metal is present in the reaction zone.

This invention comprises a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to absorb the oxygen molecule at the normal boiling point of oxygen which sieve contains at least 0.1 per cent iron, nickel, cobalt, copper, silver, gold, mercury, thallium, tin or lead or an oxide thereof in the inner adsorption region as hereinafter defined of said zeolitic molecular sieve.

The invention also comprises a process for preparing a zeolitic molecular sieve loaded with a metal which comprises contacting a molecular sieve having uniform sized pores at least large enough in cross-sectional area to absorb the oxygen molecule at the normal boiling point of oxygen with an aqueous solution of a water-soluble

salt of iron, nickel, cobalt, copper, silver, gold, cadmium, zinc, mercury, thallium, tin, lead, whereby cations of the molecular sieve are exchanged for metal cations present in said aqueous solution, removing substantially all adsorbed water from the ion-exchanged molecular sieve, and intimately contacting the dehydrated, ion-exchanged molecular sieve with a reducing agent to reduce exchanged metal cations to elemental metal.

The resulting dehydrated molecular sieve loaded with the metal may be contacted with oxygen at elevated temperature to oxidise the metal.

Zeolitic molecular sieves, both natural and synthetic, are metal aluminosilicates. The crystalline structure of these materials is such that a relatively large adsorption area is present inside each crystal. Access to this area may be had by way of openings or pores in the crystal. Molecules are selectively adsorbed by molecular sieves on the basis of their size and polarity among other things.

By the phrase "inner adsorption region" as applied to the zeolitic molecular sieves of the present invention is meant that space within the crystal lattice to which access is had only through uniform sized pores of molecular dimensions.

Zeolitic molecular sieves consist basically of three-dimensional frameworks of SiO_2 and AlO_2 tetrahedra. The tetrahedra are cross-linked by the sharing of oxygen atoms. The electrovalence of the tetrahedra containing aluminium is balanced by the inclusion in the crystal of a cation, for example, an ion of an alkali metal, and alkaline earth metal, ammonia, amine complexes, or hydrogen. One cation may be exchanged for another by conventional ion-exchange techniques. The spaces between

the tetrahedra may be occupied by water or other adsorbate molecules.

5 The zeolites may be activated by driving off substantially all of the water of hydration. The space remaining in the crystals after activation is available for adsorption of adsorbate molecules. Any of this space not occupied by reduced elemental metal atoms will be available for adsorption of
10 molecules having a size, shape, and energy of the molecular sieves.

The initial zeolite molecular sieves to be useful in the present invention, must be capable of adsorbing oxygen molecules at
15 the normal boiling point of oxygen. Included among these are the natural zeolitic molecular sieves, chabazite, faujasite, erionite, mordenite, gmelinite, and the calcium form of analcite, and the synthetic
20 zeolitic molecular sieves, zeolites A, D, L, R, S, T, X and Y. The natural materials are described in the mineralogical handbooks and texts. The characteristics of the synthetic materials and processes for making them are shown in the following Patents
25 and Patent Applications.

Zeolite A is described and claimed in Patent No. 777,232.

30 Zeolite D is described and claimed in Patent Application No. 27153/58 (Serial No. 868,846).

Zeolite L is described and claimed in Patent Application No. 1501/59 (Serial No. 909,264).

35 Zeolite R is described and claimed in Patent Application No. 21151/58 (Serial No. 880,702).

40 Zeolite S is described and claimed in Patent Application No. 8316/59 (Serial No. 909,265).

Zeolite T is described and claimed in Patent Application No. 13933/59 (Serial No. 912,936).

45 Zeolite X is described and claimed in Patent No. 777,233.

Zeolite Y is described and claimed in Patent Application No. 11328/59 (Serial No. 909,266).

50 In accordance with the process of the present invention, a zeolitic molecular sieve capable of adsorbing a substantial amount of oxygen at the normal boiling point of oxygen is ion exchanged by contacting the molecular sieve with an aqueous solution
55 of a water-soluble salt of the metal to be reduced to the elemental state. When sufficient ion exchange occurs, the exchange zeolite is removed from contact with the exchanging solution and heated for example
60 to a temperature of about 350° C. in a flowing stream of inert, dry gas or in a vacuum. The activated molecular sieve is then ready for reduction of the cations to the elemental metal. It has been found
65 that the most satisfactory dispersion of the

elemental metal throughout the adsorption region of the zeolitic molecular sieves is obtained if substantially all of the water is removed from the molecular sieves prior to the reduction step. When the molecular
70 sieves are only partially dehydrated, the products are still usable, but will not have the metal as well dispersed, thereby reducing the specific surface of the metal in the molecular sieves with a corresponding reduction
75 in the surface activity of the contained metal.

The activated molecular sieve is then treated with a reducing agent. Alkali metal vapors or preferably gaseous hydrogen, are suitable reducing agents for the process of the present invention. The reduction may be accomplished by passing the gaseous or
80 vaporous reducing agent through a bed of the ion-exchanged, activated zeolitic molecular sieves. In the case of the alkali metals, it is sufficient to mix the molten metals with the ion-exchanged activated zeolite; sufficient vapors are given off by the molten metal to effect the reduction.
90

The reduction should be effected in an inert atmosphere as should be the subsequent cooling of the material. The maximum temperature of reduction must be below the temperature at which the crystal
95 structure of the zeolitic molecular sieve is destroyed, i.e. 650° C. or preferably 500° C.

The metals which may be loaded into the zeolitic molecular sieves by the present process are copper, silver, gold, zinc,
100 cadmium, mercury, thallium, tin, lead, iron, cobalt, and nickel.

EXAMPLE I.

Zeolite X (100 grams) was placed in a 16-millimeter inside diameter glass column
105 to a bed depth of 70 centimeters. A 0.22 molar nickel nitrate solution (128 grams $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 2 liters water) was passed up through the column at a rate of 10 milliliters per minute. The zeolite was
110 washed after completion of exchange by passing 500 milliliters distilled water through the column. The zeolite was then removed from the column and dried at 100° C. X-ray diffraction analysis showed
115 the crystal structure of the zeolite to be intact.

The nickel-exchanged zeolite was placed in a vertical tube and heated under a hydrogen purge of 0.5 cubic feet per hour
120 at 300–350° C. for three hours until dehydrated. The temperature was then increased to 500° C. for three hours while still under hydrogen purge to accomplish hydrogen reduction of the nickel-exchanged
125 zeolite. The zeolite was then cooled overnight under 5 psig hydrogen. The product was uniformly black and X-ray diffraction analysis of the zeolite indicated the presence

of elemental nickel. Chemical analysis of the product indicated 8.6 weight per cent nickel.

EXAMPLE II.

5 Zeolite X powder (314 grams) was slurried at room temperature with two liters of 0.2 molar silver nitrate (containing 68 grams AgNO_3). After the exchange reaction was complete, the zeolite was washed with water until the wash effluent was free of silver-ions. The zeolite was then dried at 110° C. Chemical analysis of the zeolite indicated the presence of 11.3 per cent silver.

15 The silver-exchanged zeolite X was heated in a nitrogen purge at 350° C. for 2 hours. After cooling the zeolite to 200° C., hydrogen was admitted at about 1 cubic foot per hour and the heating continued for one hour. The white silver-exchanged zeolite X turned black in the presence of hydrogen. An exposure of the silver-loaded zeolite X to air, after reduction, changed the color from black to yellow-brown. X-ray diffraction analysis of the product after reduction showed the crystal structure to be intact and the elemental silver present had a particle size of less than 10^{-6} centimeters.

EXAMPLE III.

30 A solution of mercuric nitrate was prepared by dissolving 90 grams of $\text{Hg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in one liter of water. About 6 grams of NaNO_3 was added to a buffering agent and concentrated acetic acid was added until the solution was clear.

35 Zeolite X powder (100 grams) was slowly added to the above solution and then allowed to stand for 1½ hours. The zeolite was then filtered, washed and dried at 100° C. for two hours.

40 The mercury-exchanged zeolite containing 57.4 weight per cent mercury was placed in a horizontal tube furnace and heated under a hydrogen purge of 5 cubic feet per hour. The bed was heated at 100° C. for 1½ hours and then allowed to cool overnight. The bed was then heated at 110—200° C. for 1½ hours, then at 200—220° C. for five hours, all under a hydrogen purge of 5 cubic feet per hour. The bed was cooled overnight and then heated at 200—350° C. for 2½ hours under a hydrogen purge of 5 cubic feet per hour and allowed to cool to room temperature. The bed color changed from yellow to gray during the action. Even though an appreciable amount of mercury was distilled out of the zeolite, the zeolite product contained 2.5 weight per cent mercury.

EXAMPLE IV.

A solution of cadmium nitrate was pre-

pared by dissolving 80 grams of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in one liter of distilled water. This solution was mixed with 100 grams of zeolite X and allowed to stand for 2½ hours. The zeolite was then filtered and dried at 100° C. for two hours.

65 The cadmium-exchanged zeolite containing 177.9 weight per cent cadmium was placed in a horizontal tube furnace and heated at 90—230° C. for two hours under 2—3 cubic feet per hour hydrogen. The bed color changed from white to yellow. Chemical analysis of the zeolite product indicated that it contained 16.6 weight per cent cadmium. On further heating at temperatures up to 550° C. for 5½ hours some of the cadmium metal was distilled out. The zeolite color turned to white, and the cadmium content dropped to 14.8 per cent.

EXAMPLE V.

85 A solution of lead nitrate was prepared by dissolving 86 grams of $\text{Pb}(\text{NO}_3)_2$ in one liter of distilled water. This solution was then slurried with 100 grams of zeolite X for one hour. The zeolite was then filtered and dried at 100° C. Chemical analysis indicated that the lead-exchanged zeolite X contained 31.4 weight per cent lead.

90 The lead-exchanged zeolite was placed in a horizontal tube furnace and heated under 2 cubic feet per hour hydrogen at 110—360° C. for 1½ hours and at 200—475° C. for seven hours. The bed color changed from white to black. Chemical analysis of the product indicated that it contained 36.4 weight per cent lead. X-ray diffraction analysis of the product showed that the crystal structure was intact and elemental lead was present.

EXAMPLE VI.

105 A solution of copper nitrate was prepared by dissolving 12.1 grams $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in one liter of distilled water. This solution was mixed with 100 grams of zeolite X and allowed to stand for ten minutes. The zeolite was filtered and dried overnight at 100° C.

110 The copper-exchanged zeolite containing 3.0 weight per cent copper was placed in a horizontal tube furnace and heated under 2 cubic feet per hour hydrogen at 100—265° C. for eight hours and then at 235—450° C. for four hours. The bed color changed from light blue to pink-rose. Chemical analysis of the dried product indicated 3.5 weight per cent copper. X-ray diffraction analysis of the product showed no crystallographic decomposition.

EXAMPLE VII.

120 A solution of iron nitrate was prepared by dissolving 20.2 grams $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in one liter distilled water. This solution

was slurried with 100 grams zeolite X and allowed to stand for ten minutes. The zeolite was filtered and dried at 100° C. for three hours.

- 5 This iron-exchanged zeolite containing 2.4 weight per cent iron was then placed in a horizontal tube furnace and heated under 2 cubic feet per hour hydrogen at 100—320° C. for ten hours. The bed color
10 changed from yellow-brown to gray-brown. Chemical analysis of the product indicated 3.2 weight per cent iron. X-ray diffraction analysis of the product showed no crystallo-
graphic decomposition.

EXAMPLE VIII.

- 15 Zeolite A powder (80 grams) was slurried at room temperature into 860 milliliters of 0.2 M silver nitrate solution (contained 28.2 grams AgNO_3). The mixture was allowed
20 to stand about $\frac{1}{2}$ hour and was then filtered. The solid was then washed with water until free of silver. The solid was then dried at 100° C.

- 25 The silver-exchanged zeolite A containing 19.9 weight per cent silver was placed in horizontal tube furnace and dehydrated by heating at 350—400° C. for 1 $\frac{1}{2}$ hours. The zeolite was then cooled to room temperature. Hydrogen (0.5 cubic feet per
30 hour) was passed through the bed for 20 minutes. The bed turned yellow-brown. The zeolite was heated to 100—200° C. while passing hydrogen through it for 25 minutes. The product had a uniformly
35 dark brown color and contained 23.5 weight per cent silver. X-ray diffraction analysis of the silver A zeolite after reduction indicated that hydrogen exchange had occurred and that elemental silver was present.

EXAMPLE IX.

- 40 A sample of mordenite (in the form of beach pebbles found in Nova Scotia) with an approximate composition of $\text{RO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ where R is $(\text{Na}^+)_2$ and Ca^{++}
45 was ground to pass through a 150 U.S. Standard mesh screen. A 7.6 gram portion of this powder was mixed with 150 milliliters aqueous solution containing 1.5 grams of silver nitrate. This mixture was
50 allowed to stand with frequent agitation for 1 $\frac{1}{2}$ hours. It was then filtered and washed with water until the filtrate gave a negative test for silver ion. The zeolite was dried at 110° C.

- 55 The silver-exchanged mordenite was placed in a horizontal tube furnace and heated at 350° C. for 3 hours in a stream of hydrogen gas. Chemical analysis of the product indicated that it contained 9.3
60 weight per cent silver. The structure of the crystal was indicated by X-ray diffraction techniques to be a hydrogen-exchanged form of mordenite.

EXAMPLE X.

A quantity (15 grams) of sodium zeolite X powder was put into 50 milliliters of an aqueous solution of thallous sulphate (18 grams per liter of solution) and the suspension was stirred for 20 minutes. The zeolite powder was filtered from the solution and washed with distilled water. The washed zeolite was then dehydrated by heating to 375° C. under reduced pressure. A few grams of the activated, thallous-exchanged, zeolite powder were mixed with a few grams of metallic sodium in a 250 ml. flask and heated to a temperature in the range of 150° C. to 180° C. with continuous stirring under an argon atmosphere. The final product was black in color and contained 31 weight per cent of thallium. The presence of thallium metal was confirmed by X-ray.

The processes illustrated by Examples I to X can be employed to make a metal-containing zeolitic molecular sieve only when a suitable stable cation of the metal to be introduced into the molecular sieve is available. This requirement cannot always be met. For example, platinum occurs in simple ionic salts in the anionic part of the salt. Thus the usual cation-exchange techniques for introducing platinum into the crystal structure of a zeolite molecular sieve cannot be employed. In some instances, notably with chromium ions, the simple cation is not stable except in acidic solutions which destroy the crystal structure of the zeolitic molecular sieve.

In the previous examples, the reducing agents are oxidized to cations which take up the position in the zeolitic molecular sieve structure formerly occupied by the cation which was reduced. However, it has been found that zeolitic molecular sieve cations may be reduced by reducing agents which are not oxidized to cations even though there are no obvious cations to replace them. This may be illustrated by the following examples.

EXAMPLE XI.

Hydrated Cu(II) X zeolite (15 grams) containing 12.2 weight per cent Cu on an anhydrous basis was placed in a 1 inch "Pyrex" tube ("Pyrex" is a Registered Trade Mark). The tube was controlled at 375° C. in a split tube furnace for 2 $\frac{1}{2}$ hours in a stream of nitrogen. The tube was then cooled to 350° C. and a stream of carbon monoxide was continued for 2 $\frac{1}{2}$ hours during which time the zeolite changed from light blue to light purple. The tube was then cooled to 350° C. and a stream of carbon monoxide was continued for 2 $\frac{1}{2}$ hours during which time the zeolite changed from light blue to light purple. This color change is indicative of reduction. The

sample was cooled in nitrogen. It was removed and submitted for analysis without exposure to air. The analysis showed 9.4 weight per cent copper metal on an anhydrous basis.

A sample of the same starting zeolite was treated under identical conditions of temperature and time with hydrogen instead of carbon monoxide. The reduction took place much more rapidly than with carbon monoxide. Analysis of this sample showed 9.8 weight per cent copper metal on an anhydrous basis.

In this case, it is believed that hydrogen ions were obtained from residual water remaining in the zeolitic molecular sieve after the activation step.

EXAMPLE XII.

Hydrated Cu(II) X zeolite (25 grams) containing 12.2 weight per cent Cu on an activated basis was suspended in 200 ml. distilled water in a 500 ml. 3-necked flask fitted with a condenser, a thermometer, and a stirrer. An inert atmosphere was maintained over the suspension. Hydrazine hydrochloride (5.25 grams, .05 moles) was added to the suspension. A solution of sodium hydroxide (4.0 grams, .1 moles) was added dropwise over a period of 30 minutes. Copious amounts of gas, presumably nitrogen, were evolved. The zeolite first turned colorless, probably forming the copper (I) X zeolite, and then deep red brown. The mixture was heated to 100° C. to ensure complete reaction and destruction of excess hydrazine. The zeolite was filtered and washed with water and acetone under an inert atmosphere. It was extremely reactive in air, turning light blue in a few minutes. A sample was heated to 350° C. in vacuo for 2½ hours. No visible change occurred. Analysis showed 8.1 weight per cent copper metal on an anhydrous basis and less than 0.1 per cent nitrogen.

It is a simple matter to obtain metal oxide-loaded molecular sieves from the metal-loaded molecular sieves by standard oxidation procedures. Exposure of the metal-loaded molecular sieve to oxygen at an elevated temperature is quite satisfactory. However, the temperature should not exceed the temperature at which the crystal structure of the zeolitic molecular sieve will be destroyed.

The maximum metal that may be incorporated in the zeolitic molecular sieves by the process of the present invention is limited by the extent to which the molecular sieves may be ion-exchanged with the desired cations. However since the metals are distributed throughout the molecular sieves according to the location of the ion-exchange site of the crystals, it is possible

to obtain a high degree of dispersion of the metal throughout the crystals and the contained metal has a very high specific surface.

The products produced by the process of the present invention are quite useful as catalysts, and particularly as selective catalysts for the specific catalysis of reactants which are mixed with other materials which are not adsorbed by the zeolitic molecular sieve. The adsorbed materials react leaving the non-adsorbed materials unreacted.

Similarly, the products are useful as selective getters, gettering certain components of a mixture without affecting the other components.

The metal-containing zeolite molecular sieves are useful as a means for effecting the controlled addition of metals to reaction systems.

Still another advantage of the use of metal-loaded zeolite molecular sieves resides in the fact that the tendency for the metal to migrate is minimized. Normal catalysts consisting of supported metals exhibit migration of the metal during catalysis thereby giving rise to unequal distribution of catalyst material with a corresponding decrease in catalytic effectiveness.

As used herein the term "activation" is employed to designate the removal of water from the zeolitic molecular sieves, i.e. dehydration, and does not refer to catalytic activity. The zeolitic molecular sieves containing the elemental metal exhibit catalytic activity.

The process of the present invention provides materials having surface areas about four times that expected with most alumina, silica or aluminosilicate supported metals thereby providing a greater surface area available for reaction. Since the external surface of the molecular sieve represents less than 1 per cent of the total surface area it may be seen that there is an extremely large area available for chemisorption and catalysis in the internal portion of the molecular sieve. Since this region is available only through pores of molecular size it may be seen that selective chemisorption and catalysis may be obtained in a system containing a mixture of molecules some of which are too large to enter the pores whereas others are capable of entering the pores.

Co-pending Application No. 32330/59 (Serial No. 937,749) discloses and claims a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule, which sieve contains platinum, aluminum, chromium, molybdenum, tungsten, manganese, rhenium, titanium, zirconium, hafnium, vanadium, iron, cobalt, nickel, copper or oxides of these metals in

the inner adsorption region (as therein defined) of said zeolitic molecular sieve.

Co-pending Application No. 32330/59 (Serial No. 937,749) also discloses and claims a process for preparing a zeolitic molecular sieve loaded with a metal or oxide thereof, comprising contacting a dehydrated molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule (as therein defined) with a fluid, decomposable compound of copper, silver, gold, platinum, iridium, osmium, palladium, rhodium, ruthenium, zinc, cadmium, aluminum, tin, lead, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, titanium, zirconium, hafnium or vanadium, whereby said decomposable compound is adsorbed into the inner adsorption region (as therein defined) of said molecular sieve and decomposing said decomposable compound to the elemental metal.

Co-pending Application No. 32329/59 (Serial No. 937,748) discloses and claims a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule, which sieve contains at least 0.1% by weight of gold, iridium, osmium, palladium, rhodium, or ruthenium or an oxide thereof in the inner adsorption region (as therein defined) of said zeolitic molecular sieve.

Co-pending Application No. 32329/59 (Serial No. 937,748) also discloses and claims a process for producing a zeolitic molecular sieve loaded with a metal or oxide thereof which comprises contacting a molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule with an aqueous solution of a complex cation comprising an amine or ammonia and copper, silver, gold, chromium, zinc, cadmium, tin, lead, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, or platinum, whereby cations of the molecular sieve are exchanged for said complex cations, removing substantially all the adsorbed water from the ion-exchanged molecular sieve in an inert atmosphere, and reducing said complex cations in said dehydrated molecular sieve to the elemental metal.

We make no claim to a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule, which sieve contains iron, nickel, cobalt, copper or oxides of these metals in the inner adsorption region as claimed in co-pending Application No. 32330/59 (Serial No. 937,749).

We also make no claim to a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule, which sieve contains gold, or an oxide thereof in the inner adsorption region as claimed in co-pending Application No. 32329/59 (Serial No. 937,748).

Subject to the foregoing disclaimers,
WHAT WE CLAIM IS:—

1. A dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the oxygen molecule at the normal boiling point of oxygen which sieve contains iron, nickel, cobalt, copper, silver, gold, mercury, thallium, tin or lead or an oxide thereof in the inner adsorption region as hereinbefore defined of said zeolitic molecular sieve.
2. A dehydrated molecular sieve as claimed in Claim 1 substantially as hereinbefore described with reference to and as illustrated in the examples.
3. A process for preparing a zeolitic molecular sieve loaded with a metal which comprises contacting a molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the oxygen molecule at the normal boiling point of oxygen with an aqueous solution of a water-soluble salt of iron, nickel, cobalt, copper, silver, gold, cadmium, zinc, mercury, thallium, tin, lead, whereby cations of the molecular sieve are exchanged for metal cations present in said aqueous solution, and intimately contacting the dehydrated, ion-exchanged molecular sieve with a reducing agent to reduce exchanged metal cations to elemental metal.
4. A process as claimed in Claim 3 in which the ion-exchanged molecular sieve is dehydrated prior to contact with the reducing agent.
5. A process as claimed in Claim 3 in which the exchange metal cation is reduced to elemental metal by contacting the ion-exchanged molecular sieve with a reducing agent in an aqueous layer.
6. A process as claimed in any of Claims 3 to 5 in which the zeolitic molecular sieve loaded with copper, silver, gold, mercury, thallium, tin, lead, iron, nickel, cobalt, cadmium or zinc is contacted with oxygen atoms at elevated temperature to oxidize the metal.
7. A process as claimed in Claim 3 for preparing a zeolitic molecular sieve loaded with a metal substantially as hereinbefore described with reference to and as illustrated in any of the examples.

8. A dehydrated zeolitic molecular sieve loaded with a metal when prepared by the process as claimed in any of Claims 3 to 7.

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12 Church Street,
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Chartered Patent Agents.

Abingdon : Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1963.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2,
from which copies may be obtained.

